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⑩ 日本国特許庁(JP)

⑪ 特許出願公開

⑫ 公開特許公報(A)

昭60-121207

⑬ Int.Cl.<sup>4</sup>

識別記号

庁内整理番号

⑭ 公開 昭和60年(1985)6月28日

B 22 F 9/28

7141-4K

審査請求 未請求 発明の数 1 (全4頁)

⑮ 発明の名称 超微粒子の製造方法

⑯ 特 願 昭58-225363

⑰ 出 願 昭58(1983)12月1日

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Added  
to the Opposition List July 28, 2004  
Publication No.  
Patent and Trademark Office  
31925 Muroga, Asahi-ku, A

明 細 書

## 1 発明の名称

超微粒子の製造方法

## 2 特許請求の範囲

1. ハロゲン化ニオブとナトリウムを気相で反応させることによる超微粒子ニオブの製造方法。
2. 反応を、副生するハロゲン化ナトリウムの沸点以下の温度でおこなう特許請求の範囲第一項記載の方法。
3. ハロゲン化ニオブを反応室に高線速度で導入する特許請求の範囲第一項、第二項記載の方法。
4. ハロゲン化ニオブを1m/秒以上の線速度で反応室に導入する特許請求の範囲第三項記載の方法。

## 3 発明の詳細な説明

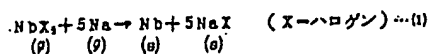
本発明はハロゲン化ニオブとナトリウム(以下 $\text{Na}$ という)を気相で反応させ、金属ニオブの超微粒子を効率よく製造する方法に関するものである。ここで云う超微粒子とは粒径 $1\mu$ 以下の粉体をいう。超微粉体は、その微細さゆえその性質はバルク状態とはまったく異なり新しい用途が期待されている。

金属超微粉の製造方法は物理的方法としてはアトマイズ法やガス中蒸発法が、化学的方法としては熱分解法やガス還元法、気相反応法が知られている。気相反応は金属塩化物等の蒸気を $\text{H}_2$ 、 $\text{CO}$ 等により還元して微粉体を得る方法で、この方法は連続操業が可能な反面 $\text{H}_2$ 、 $\text{CO}$ の還元力が弱く、超微粉化し得る対象物質が限定される欠点があった。又この方法は反応温度も比較的高温にする必要があった。

またガス蒸発法では、蒸気圧の低い高融点金属( $\text{Nb}$ ,  $\text{Ta}$ ,  $\text{Mo}$ ,  $\text{W}$ など)では超微粒子の製造自体がわけて困難であった。

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一般に気相反応法で超微粒子をうるためには、高い過飽和度比（実際の蒸気圧／平衡蒸気圧）を實現して核生成速度を早めることが必要である。本発明でのハロゲン化ニオブとナトリウムとの還元反応は次式で示される



気相反応で生成物はすべて固体である。従って温度領域が広いため高い過飽和度比が安定してえられ、又強い還元力を有し、比較的蒸気圧の高いNaを使用するため反応速度も早い。

また反応器の構造、反応ガスの導入方法、加熱方法などの装置因子も超微粒子製造のための大きな因子である。

本発明者らは、これらを勘案して効率よくニオブの超微粒子を得る方法をもとめて研究した結果本発明を完成したものである。

次に本発明を詳述する。ハロゲン化ニオブとNaを各々不活性ガス中で気化させ、反応温度に維持してある反応室に、はじめにNa蒸気を次いでハロ

ゲン化ニオブを早い線速度で送り込む。ここで用いるハロゲン化ニオブとしては塩化ニオブ（以下NbCl<sub>5</sub>という）、臭化ニオブ（以下NbBr<sub>5</sub>という）、碘化ニオブ（以下NbI<sub>5</sub>という）、弗化ニオブ（以下NbF<sub>5</sub>という）およびこれらの低級ハロゲン化物いずれをもちいても粒径1μ以下の金属ニオブがえられる。

次に本発明につきNbCl<sub>5</sub>を用いた例をもとに更に詳述する。NbCl<sub>5</sub>とNaの量比は(1)式に示したごとくモル比で1:5が当量であり、本発明においても当量であれば事実上よいが好ましくは0.5~2.0当量、さらに好ましくは0.8~1.2当量の範囲で反応させることが望ましい。なぜなら0.8当量より小ではNbCl<sub>5</sub>の損失が大きくなり、1.2当量より大では不経済であるばかりか過剰のNa処理が繁雑となるからである。

反応は300℃以上で開始するので、反応温度は300℃以上であればよく、上限温度は核生成速度を早くするため副生するNaClの沸点1400℃以下であることが好ましく、特に好ま

しくはその融点の800℃以下である。前記融点以下で反応させることにより、粒径が均一な粒子がえられる。

気化したNbCl<sub>5</sub>は露点以上の温度に保ち、あらかじめNa蒸気が導びかれている反応室内に高速で送り込むことが好ましい。

反応室へ吹き出す速度は超微粉の<sup>成</sup>微生物を得る上で高勢速度で導入することがよく、1m/sec以上であれば特に限定されないが反応室の長さの制限から3m/sec以下が望ましい。

反応は通常大気圧でみなわれるが装置面から許されるならば減圧下もしくは加圧下でみこなりことも可能である。

生成した超微粉のニオブ、副生するNaClおよび過剰のNaの捕集するときの温度条件は特に限定されないが、100℃以上に保ち捕集しながらNaを分離しても0℃以下に冷却して捕集してもよい。

捕集した生成物は水を含まない有機溶剤を用いてNaおよびNaClを除去することが簡便である。洗浄後有機溶剤の付着している超微粒子は50℃

以下の酸素を含む不活性ガス中もしくは乾燥空気中で乾燥することにより、超微粒子の表面に酸化膜を生成させ安定化させることができる。

本発明によれば高収率で0.05~0.2μmの金属ニオブがえられる。

又、比較的低温での瞬間的な反応であるため、きわめて効率よく生産できる。

更に還元剤のナトリウムも比較的安価なので<sup>経</sup>費性にすぐれている。

次に実施例で本発明を更に詳述する。

#### 実施例1

市販のフェロニオブを塩素化して常法により不純物を除去してえた純度99.9%のNbCl<sub>5</sub>600gをNbCl<sub>5</sub>ホッパー<sup>に</sup>仕込んだ。

市販Naを気化器で760℃に保ち11L/minのArガスをキャリアーとしてNa蒸気(Na5g/min)を800℃に保った縦型の反応室上部より導入した。一方、NbCl<sub>5</sub>はホッパーからスクリー<sup>ン</sup>で300℃に保った気化室に10g/minで送り気化

させ、 $\text{NbCl}_5$ を1 L/minのArで反応室内にノズルをとうして1 m/secの線速度をもって導入した。

Naの割合は $\text{NbCl}_5$ の1.2倍当量であった。

反応室下部の出口から捕集器に導びかれたNb超微粉、ナトリウムおよび塩化ナトリウムの混合物は反応終了後捕集器ごと反応器からはずしてエチルアルコール1 Lを加えNaを溶解させ沈降分離でエチルアルコールを除去した。ここでえられたスラリーにエチレングリコール9 Lを加え $\text{NaOH}$ を溶解させ、沈降分離でニオブ超微粉を分離エチルアルコールで洗浄した。

エチルアルコール中の超微粉スラリーは、室温の乾燥空気中でエチルアルコールを気化させ超微粉の表面を酸化安定化した。

えられた超微粉ニオブは次の様であった。

収量	180 g (収率87%)
粒度	0.05 ~ 0.1 $\mu\text{m}$
Nb	94.4%
O	5.6%
0.2	0.1%

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超微粒子ニオブの電子顕微鏡写真( $\times 50000$ )を図1に示した。

#### 実施例2

実施例1で使用した装置を用いて $\text{NbCl}_5$ とNaを反応させた。

$\text{NbCl}_5$ を8.3 g/minの割合で気化させノズルより反応室にふきこんだ。同時にNa蒸気を2 g/minの割合で600℃に保った反応室に通した。キャリアーとしてのArガスは各々2 L/min, 1.5 L/minであった。

生成した超微粉は2アミノエタノール1.5 L, エタノール3 Lを使用してNaおよびNaBrを除去するとともに安定化した。

収率	90%	85%
Nb	92%	
O	8%	
Br	2.4%	
粒径	0.2 $\mu\text{m}$	

図2にえられた超微粉の電子顕微鏡写真( $\times 10000$ )

を示した。

#### 4 図面の簡単な説明

図1は $\text{NbCl}_5$ とNaの反応でえられた超微粒子の電子顕微鏡写真( $\times 50000$ )

図2は $\text{NbCl}_5$ とNaの反応でえられた超微粒子の電子顕微鏡写真( $\times 10000$ )である。

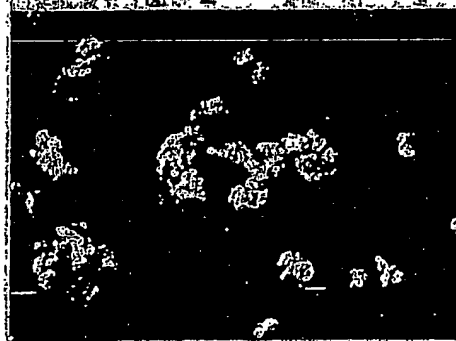
特許出願人 東洋曹達工業株式会社

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図 1



図 2



## TRANSLATION

Unexamined Published Japanese Patent Application  
No. S60-121207

## Title of the Invention:

Process for Producing Ultrafine Particles

Publication Date: June 28, 1985

Patent Application No. S58-225363

Filing Date: December 1, 1983

Applicant: Tosoh Corporation

Inventor: H. Sudo, I. Hirano and K. Nishizawa

## 1. TITLE OF THE INVENTION

Process for Producing Ultrafine Particles

## 2. CLAIMS

1. A process for producing ultrafine particulate niobium, comprising reacting a niobium halide with sodium in a gaseous phase.

2. The process as claimed in claim 1, wherein the reaction is performed at a temperature not higher than the boiling point of sodium halide which is generated as a by-product.

3. The process as claimed in claim 1 or 2, wherein the niobium halide is introduced into a reaction chamber at a high linear velocity.

4. The process as claimed in claim 3, wherein the niobium halide is introduced into a reaction chamber at a linear velocity of at least 1 m/sec.

## 3. DETAILED DESCRIPTION OF THE INVENTION

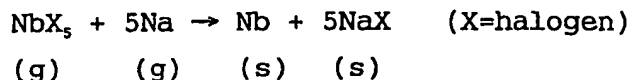
The present invention relates to a process for efficiently producing ultrafine particles of metal niobium by reacting a niobium halide with sodium (hereinafter referred to as "Na") in a gaseous phase. The term "ultrafine particle powder" as used herein means a powder having a particle size of 1  $\mu$ m or less. Owing to the fineness, ultrafine powder materials

exhibit properties utterly different from those in the bulk state and are expected to bring new uses.

With respect to the process for producing metal ultrafine powder, physical processes such as atomization and evaporation in gas, and chemical processes such as thermal decomposition, gas reduction and gas phase reaction are known. The gas phase reaction is a process of reducing a vapor of a metal chloride or the like by  $H_2$ , CO or the like to obtain a fine particle material. According to this process, a continuous operation can be performed, however, the objective material which can be formed into ultrafine powder is disadvantageously limited because  $H_2$  or CO is weak in the reducing power. Furthermore, this process requires a relatively high reaction temperature.

According to the gas evaporation process, in the case of a high melting point metal (e.g., Nb, Ta, Mo, W) having a low vapor pressure, the production itself of ultrafine particles is very difficult.

In general, for obtaining ultrafine particles by a gas phase reaction, it is necessary to realize a high oversaturation degree ratio (i.e., actual vapor pressure/equilibrium steam pressure) and thereby elevate the nucleation rate. The reducing reaction between a niobium halide and sodium in the present invention proceeds as shown in the following scheme (1):



In the gas phase reaction, all products are obtained as solid. Therefore, the temperature region is broad and a high oversaturation degree ratio can be stably obtained. Furthermore, since Na used has a strong reducing power and a relatively low vapor pressure, the reaction proceeds at a high rate.

In addition, the structure of reactor, the method of introducing the reaction gas, the heating method and other structural factors are also important factors in the production of ultrafine particles.

By taking account of these, the present inventors have

made studies for a method of efficiently obtaining ultrafine particulate niobium, as a result, they have accomplished the present invention.

The present invention will be described in detail below. A niobium halide and Na each is vaporized in an inert gas. Thereafter, Na steam and then a niobium halide are fed at a high linear velocity into a reaction chamber maintained at a reaction temperature. The niobium halide used here may be any of niobium chloride (hereinafter referred to "NbCl<sub>3</sub>"), niobium bromide (hereinafter referred to as "NbBr<sub>3</sub>"), niobium iodide (hereinafter referred to as "NbI<sub>3</sub>"), niobium fluoride (hereinafter referred to as "NbF<sub>3</sub>") and lower halides thereof. Whichever is used, a metal niobium having a particle size of 1  $\mu$ m or less can be obtained.

In the following, the present invention is described in detail by specifically referring to the case where NbCl<sub>3</sub> is used. With respect to the ratio between NbCl<sub>3</sub> and Na, the equivalent is, as shown in scheme (1), 1:5 in terms of a molar ratio. In the present invention, it may be sufficient in practice if the ratio is equivalent, however, the reaction is preferably performed at a ratio of from 0.5 to 2.0 equivalent, more preferably from 0.8 to 1.2 equivalent. If the ratio is less than 0.8 equivalent, the loss of NbCl<sub>3</sub> increases, whereas if it exceeds 1.2 equivalent, not only this is unprofitable but also a cumbersome treatment for excess Na is necessary.

The reaction starts at 300°C or higher, therefore, the reaction temperature is suitably 300°C or higher and in order to increase the nucleation rate, the upper limit of the temperature is preferably not higher than the boiling point of NaCl, namely, 1,400°C or lower, more preferably not higher than the melting point thereof, namely, 800°C or lower. When the reaction is carried out at a temperature not higher than the melting point, particles having a uniform size can be obtained.

The vaporized NbCl<sub>3</sub> is preferably kept at a temperature not lower than the dew point and fed at a high speed into a reaction chamber where Na steam is previously introduced.

With respect to the speed in blowing the gas into the reaction chamber, the gas is preferably introduced at a high linear speed so as to obtain an ultrafine product. The blowing speed is not particularly limited as long as it is 1 m/sec or more, however, in view of the limited length of the reaction chamber, the blowing speed is preferably 3 m/sec or less.

The reaction is usually performed under atmospheric pressure, however, if the equipment allows, the reaction may be performed under reduced or increased pressure.

At the time of collecting the produced ultrafine niobium powder, the by-product NaCl and the excessive Na, the temperature condition is not particularly limited and Na may be separated while collecting those by keeping the temperature at 100°C or higher, or those may be cooled to 0°C or lower and then collected.

From the products collected, Na and NaCl can be easily removed using an organic solvent not containing water. After the rinsing, the ultrafine particle having attached thereto the organic solvent is dried in an inert gas or dry air containing oxygen at 50°C or lower to form an oxide film on the surface of the ultrafine particle, so that the ultrafine particle can be stabilized.

According to the present invention, metal niobium of a particle diameter of from 0.05 to 0.2  $\mu\text{m}$  can be obtained in a high yield.

Furthermore, this is an instantaneous reaction occurring at a relatively low temperature, therefore, the production can be attained with extremely high efficiency.

In addition, sodium as a reducing agent is relatively inexpensive, therefore, the production cost is low.

The present invention is described in greater detail below by referring to the following Examples.

#### Example 1

600 g of NbCl<sub>5</sub> having a purity of 99.9% which was obtained by chlorinating a commercially available ferroniobium and removing impurities in a usual manner, was charged into an



NbCl<sub>5</sub> hopper.

A commercially available Na was kept at 760°C in a vaporizer and the Na vapor (Na: 5 g/min) was introduced from the upper portion of a vertical reaction chamber kept at 800°C using 11 λ/min of Ar gas as a carrier gas. On the other hand, NbCl<sub>5</sub> was fed from the hopper to a vaporizing chamber kept at 300°C at 10 g/min by means of a screw. The NbCl<sub>5</sub> was then introduced into the reaction chamber through a nozzle at a linear velocity of 1 m/sec using 1 λ/min of Ar.

The ratio of Na was 1.2 times equivalent to NbCl<sub>5</sub>. A mixture of Nb ultrafine powder, sodium and sodium chloride was guided from the outlet at the lower portion of the reaction chamber to a collector and after the completion of reaction, the collector as a whole was taken off from the reactor. To the mixture, 1 λ of ethyl alcohol was added to dissolve Na and the ethyl alcohol was removed by sedimentation. To the resulting slurry, 9 λ of ethylene glycol was added to dissolve NaCl and the niobium ultrafine powder was separated by sedimentation and washed with ethyl alcohol.

The ultrafine powder slurry in the ethyl alcohol was stabilized by vaporizing the ethyl alcohol in dry air at room temperature and thereby oxidizing the ultrafine powder surface.

The thus-obtained ultrafine niobium had the following results:

Yield:	180 g (yield: 87%)
Particle diameter:	0.05 to 0.1 μm
Nb:	94.4%
O:	5.6%
Cl:	0.1%

Fig. 1 is an electron microphotograph (×50,000) of the ultrafine particulate niobium.

#### Example 2

Using the apparatus used in Example 1, NbBr<sub>5</sub> and Na were reacted with each other.

More specifically, NbBr<sub>5</sub> was vaporized at a rate of 8.3 g/min and blown into a reaction chamber through a nozzle. At

the same time, Na vapor passed through the reaction chamber kept at 600°C, at a rate of 2 g/min. In these, Ar gas as a carrier was used at a rate of 2  $\lambda$ /min and 1.5  $\lambda$ /min, respectively.

Using 1.5 liter of 2-aminoethanol and 3 liter of ethanol, Na and NaBr were removed and at the same time, the ultrafine powder produced was stabilized.

Yield:	90%, 85 g
Nb:	92%
O:	8%
Br:	n.d.
Particle diameter:	0.2 $\mu$ m

FIG. 1 is an electron microphotograph ( $\times 10,000$ ) of the ultrafine particulate niobium obtained.

#### 4. BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is an electron microphotograph ( $\times 50,000$ ) of ultrafine particles obtained by a reaction between  $\text{NbCl}_5$  and Na.

FIG. 2 is an electron microphotograph ( $\times 10,000$ ) of ultrafine particles obtained by a reaction between  $\text{NbBr}_5$  and Na.



FIG. 1

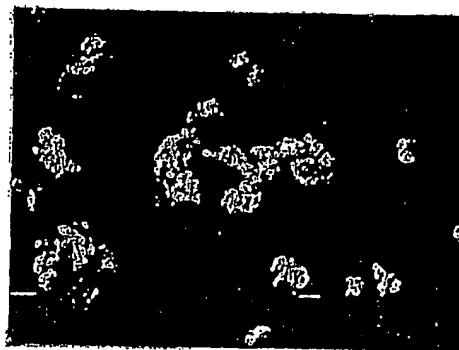


FIG. 2

## DECLARATION

Re: European Patent No. 0 946 323

I, Masako Kimura of 3-6, Namiki 7-chome, Abiko-shi, Chiba 270-1165 Japan, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a true, accurate and faithful partial translation made by me of:

Unexamined Published Japanese Patent Application  
No. S60-121207

I make this solemn declaration conscientiously believing the same to be true.

This ninth day of July, 2004

  
Masako Kimura

## HOFFMANN · EITLE

MÜNCHEN LONDON

Opposition ./ EP-B-0 946 323 Cabot Corporation

103 952 r4/cvi

**Facts and Arguments****Preamble and Summary**

All claims of the patent are attacked. The patent has independent claims in several categories, but method claim 8 is distinguished from the other independent claims by the additional technical feature

*anodizing the anode at a voltage of less than 60 volts*

which was the feature that attracted the attention of the Technical Board of Appeal in the proceedings prior to grant.

Claims 1 and 2 are "obtainable" claims, implying that the anodes they claim are incapable of characterization, except on the basis of the specific surface area of the starting powder material prior to the sintering step. This is not a good basis to define a patentable invention, because sintering changes the specific surface area and so it takes a combination of starting material parameter and sintering step characterization to fix the nature of the sintered product.

Putting it another way, the scope of claims 1 and 2 includes all sintering regimes, including regimes which create from the powder specified in claims 1 and 2 sintered anodes indistinguishable from the prior art niobium capacitor anodes.

It is only in claim 5 that we find any measure of capacitance that the anode shall deliver. However, the data in the patent reveal that this amount of capacitance is incompatible with a DC leakage low enough to meet the requirements of the independent product and use claims 1, 2, 31 and 32. The capacitance of claim 5 is not to be used to formulate the objective problem solved by the method, product and use inventions

claimed, because the patent does not provide the reader with a sufficient disclosure of how to achieve, simultaneously, the low DC leakage of claim 1 and the measure of capacitance performance of claim 5.

I. Anticipation and Obviousness of Claims 1-7 directed to a capacitor anode

I-1. Claims 1 and 2

I-1-(1) Claims 1 and 2 are anticipated by D1

D1 discloses a process for preparing a tantalum or niobium powder which provides anodes of improved properties such as required for capacitors (see the abstract, column 1, lines 10-20; column 6, lines 41-44). In Example 11 of D1, it is specifically described that "niobium powder averaged 1.2  $\mu\text{m}$  particle size according to Fisher" was produced from  $\text{K}_2\text{NbF}_7$  (column 11, lines 67-68).

D1 does not explicitly disclose a BET surface area of this niobium powder but this niobium powder has a specific surface area of at least about 0.58  $\text{m}^2/\text{g}$ , and of presumably about 1.5  $\text{m}^2/\text{g}$ . A particle having a spherical form has a minimum surface area among particles having different shapes but having the same particle size. The specific surface area of a particle having a diameter of 1.2  $\mu\text{m}$  is calculated as about 0.58  $\text{m}^2/\text{g}$  from the formula: specific surface area =  $(4\pi r^2) / [(4/3) \pi r^3 \times d]$  (r: radius of particle, d: density of niobium [8.57  $\text{g}/\text{cm}^3$ ]). Thus, the niobium powder specifically disclosed in Example 1 of D1 surely has a surface area of at least about 0.58  $\text{m}^2/\text{g}$ . We note that it is referred to in the opposed patent that "niobium metal angular powder having a Fisher Sub Sieve Size of 10.6 micrometers, .... a pre-agglomerated BET surface area of 0.17  $\text{m}^2/\text{g}$ " (page 6, lines 39-40 [0043]). If this niobium powder has a spherical form, its surface area is calculated as 0.066  $\text{m}^2/\text{g}$ . The BET surface area of 0.17  $\text{m}^2/\text{g}$  is about 2.58 times of the calculated value, 0.066  $\text{m}^2/\text{g}$ . Therefore, it can be said, that the niobium powder having a diameter of 1.2  $\mu\text{m}$ , specifically disclosed in Example 11 of D1, presumably has a specific surface area of about 1.5  $\text{m}^2/\text{g}$  (about 0.58  $\text{m}^2/\text{g} \times 2.58$ ).

An anode made from the niobium powder having a diameter of 1.2  $\mu\text{m}$  had a capacitance of 16,420  $\mu\text{C}/\text{g}$  and a residual current of 28.3,  $\mu\text{A}/\text{g}$  (D1, column 12, lines 41-42).

$$\begin{aligned}
 \text{Capacitance } 16,420 \mu\text{C/g} \\
 &= 16,420 \mu\text{FV/g} \\
 &= 16,420 \text{ CV/g.}
 \end{aligned}$$

The residual current (i.e., leakage current) of the anode is  $28.3 \mu\text{A/g}$ , and thus, its DC leakage is calculated as  $1.7 \text{ nA/CV}$  as follows.

$$\begin{aligned}
 \text{DC leakage} &= (28.3 \mu\text{A/g}) / (16,420 \text{ CV/g}) \\
 &= 0.0017 \mu\text{A/CV} \\
 &= 1.7 \text{ nA/CV}
 \end{aligned}$$

The capacitor anodes as claimed in claims 1 and 2 of the Cabot patent are clearly anticipated by the above-mentioned anode specifically disclosed in Example 11 of D1.

	<u>Claim 1</u>	<u>Claim 2</u>	<u>D1, Example 11</u>
Surface area of niobium powder ( $\text{m}^2/\text{g}$ )	$\geq 0.5$ (BET)	$\geq 0.5$ (BET)	$\geq$ about 0.58, Presumably about 1.5
DC leakage of anode (nA/CV)	less than 5.0	5.0-0.05	1.7

I-1-(2) Claims 1 and 2 are obvious in view of D1, D2, D3 and D4.

We further add the following as for the inventive step of claims 1 and 2 of the Cabot patent.

A niobium anode having a low DC leakage satisfying the DC leakage as recited in claims 1 and 2 of the Cabot patent is known as shown in D1, Example 11, as mentioned above, and in D4 as mentioned below.

D4 discloses a powder of niobium alloy for making electric capacitor (see the abstract). A niobium anode specifically disclosed in Table 8-1, penultimate line, in columns 15-16 has an anode weight of "0.920 g" and a CV/g of "7480". Leak current L is "9.9  $\mu\text{A}$ " (=9,900 nA). Leak current per g =  $9,900 \text{ nA} / 0.92 \text{ g} = 10,761 \text{ nA/g}$ .

$$\text{Thus, DC leakage} = (10,761 \text{ nA/g}) / (7480 \text{ CV/g}) = \underline{1.44 \text{ nA/CV}}$$

A niobium powder having a specific surface area satisfying the specific surface area as recited in claims 1 and 2 of the Cabot patent is known as shown in D1, Example 11, as mentioned above, and further, for example, in D2 and D3, as mentioned below.

D2 discloses a process for producing a ultrafine niobium powder (translation, page 1, claim 1). It is described that metal niobium of particle diameter of from 0.05 to 0.2  $\mu\text{m}$  can be obtained (D2, page 2, right lower column, lines 4-5 [Translation, page 4, lines 23-25]). In the working examples of D2, a niobium powder having a particle diameter of 0.05-0.1  $\mu\text{m}$  (Example 1, page 3, left upper column, line 4 from the bottom [Translation, page 5, line 26]), and a niobium powder having a particle diameter of 0.2  $\mu\text{m}$  (Example 2, page 3, right upper column, line 2 from the bottom [Translation, page 6, line 11]) are specifically disclosed. The specific surface areas of the smallest particle having a diameter of 0.05  $\mu\text{m}$  and the largest particle having a diameter of 0.2  $\mu\text{m}$  in D2 are calculated as about 14.0  $\text{m}^2/\text{g}$  and about 3.5  $\text{m}^2/\text{g}$ , respectively, provided that these particles have a spherical form. However, these particles are not spherical but have a complicated form as shown in transmission electron micrographs (D2, page 4, Fig. 1 and Fig. 2). Obviously, the niobium powders specifically disclosed in D2 have a surface area of larger than the range of about 3.5  $\text{m}^2/\text{g}$  to about 14.0  $\text{m}^2/\text{g}$ , which meets "BET surface area of at least 0.5  $\text{m}^2/\text{g}$ " as stipulated in claims 1 and 2 of the Cabot patent.

D3 discloses an ultrafine niobium power having a specific surface area of  $4.8 \times 10^4 \text{ m}^2/\text{kg}$  [ $=48 \times \text{m}^2/\text{g}$ ] (page 469, right column, Table 7), which meets "BET surface area of at least 0.5  $\text{m}^2/\text{g}$ " as stipulated in claims 1 and 2 of the Cabot patent.

For any person skilled in the art it is indispensable that undesirable DC leakage be lowered as much as possible. There is no shortage of motivation to provide a niobium capacitor anode of reduced DC leakage. As of the priority date of the Cabot patent, an ultrafine niobium powder having a specific surface area satisfying the specific surface area as stipulated in claims 1 and 2 of the Cabot patent is already known as shown in D1, D2 and D3, and further, a niobium anode having a DC leakage less than 5.0 nA/CV is also known as shown in D1 and D4. Obviously, the published state of the art, at the priority date of the claims, gave the skilled addressee the means and the motivation to manage particle size to provide the niobium capacitor anode with the performance characteristic as claimed in claim 1 or 2 of the Cabot patent.

Claims 1 and 2 of the Cabot patent lack inventive step over a combination of ultrafine niobium powder as described in D1, D2 and D3 with an anode of low DC leakage as described in D1 and D4.

**I-2. Claims 3 and 4**

It is not only well-known, but conventional, to form a dielectric film on a sintered product by anodizing the sintered product for providing an anode for capacitor (D6, col. 1, lines 16-19 and col. 2, lines 14-20). It is described in D5 that a dielectric layer formed by anodic oxidation of sintered niobium is an oxide layer composed of  $\text{Nb}_2\text{O}_5$  (i.e., niobium pentoxide) (D5, page 1113, left column, lines 3-23).

Thus, inventive step of claims 3 and 4 would be denied by combination of D1 with D5, combination of D1 through D4 with D5, or simply by the application to the specific disclosure of D1 of general knowledge of what is conventional practice.

**I-2. Claim 5**

This claim combines with the low DC leakage parameter of claim 1 an enhanced range of capacitance. This claims no more than a desirable objective. This objective is an obvious objective. The specification of an obviously desirable objective is not an invention. Specifying this problem to be solved is not in itself an invention. Incidentally, the opposed patent fails to teach how one is, simultaneously, to achieve the high capacitance of claim 5 as well as the low DC leakage of claim 1. The problem is not even solved by the opposed patent. In this way there is an insufficient disclosure of the invention of claim 5, contrary to Art. 100(b) EPC.

**I-2. Claim 6**

As for claim 6, it is described in D5 that maximum anodization voltage of a sintered product of niobium powder is 200 V (page 1111, right column, Table I), and further that anodic oxidation of the sintered product is carried out in phosphoric acid at a constant voltage of 20 V (page 1113, left column, lines 3-5).



The capacitor anode formed at a voltage of less than 60 volts, as claimed in claim 6, would lack inventive step over a combination of D1 with D5, or combination of D1 through D4 with D5.

### I-3. Claim 7

D1 through D5 are silent on a working voltage adopted for forming a niobium capacitor anode. However, in view of the description in D5 that the maximum anodization voltage of a sintered product of niobium powder is 200 V (D5, page 1111, right column, Table I), and further that anodic oxidation of the sintered product is carried out in phosphoric acid at a constant voltage of 20 V (D5, page 1113, left column, lines 3-5), and further in view of the fact that an anode formation is carried out at 80 V in aq. phosphoric acid (D1, Example 11, column 12, lines 29-31), and further in view of the fact that it is quite natural to the working voltage is lower than the forming voltage, adoption of "a working voltage of 4 to 16 volts" as in claim 7 of the Cabot patent would be a matter of routine design choice. In this technical field, it is conventional that the intended working voltage will be generally about 1/5 to about 1/2 of the voltage chosen for forming a dielectric.

D8 is concerned with capacitors of tantalum but the technical reasoning it contains at col. 2, lines 3 to 10, applies just as much to niobium as it does to tantalum, and supports the above argumentation.

For the capacitors of the technical field of the opposed patent, working voltages in the range of 4 to 16 volts are normal.

## II. Obviousness of Claims 8-28 directed to a method of forming a capacitor anode

### II-1. Claim 8

It is conventional to sinter a niobium powder and then anodize the sintered product to form a capacitor anode.

As explained above in paragraph I-1, a niobium powder used for a capacitor anode having a BET specific surface area of at least 0.5 m<sup>2</sup>/g is described in D1 (larger than about 0.58 m<sup>2</sup>/g, presumably about 1.5 m<sup>2</sup>/g; Example 11, column 11, bottom two

lines), D2 (larger than the range of about 3.5 m<sup>2</sup>/g to about 14.0 m<sup>2</sup>/g; page 2, right lower column, lines 4-5 [Translation, page 4, lines 23-25]), and D3 (4.8 x 10<sup>4</sup> m<sup>2</sup>/kg [=48 m<sup>2</sup>/g]; page 469, right column, Table 7).

It is described in D5 that maximum anodization voltage of a sintered product of niobium powder is 200 V (page 1111, right column, Table I), and further that anodic oxidation of the sintered product is carried out in phosphoric acid at a constant voltage of 20 V (page 1113, left column, lines 3-5).

Thus, it would be obvious to sinter a niobium powder as described in D1, D2 or D3, and then, anodize the sintered product at a voltage of less than 60 volts, for example, at 20 volts as taught in D5, to form a capacitor anode. Claim 8 would lack inventive step over a combination of D5 with any one of D1, D2 and D3.

## II-2. Claims 9-11

It is described that sintering is carried out "at temperatures ranging from 1000°C to 1550°C" in D5 (page 1112, right column, lines 14-17 below Table II); and "at a corrected temperature of 1500°C" in D1 (column 12, lines 28-29).

Further, D7 discloses a process for making a capacitor anode from an oxygen-containing niobium powder which includes a step of sintering pellets, made from the powder, at a temperature ranging from 1600 to 2200°C (D7, col. 1, line 70 to col. 2, line 9).

The sintering temperatures as described in D5, D1 and D7 meet the sintering temperatures of "from 1200 to 1750°C", "from 1200 to 1400°C" and "from 1250 to 1350°C", stipulated in claims 9, 10 and 11, respectively. Thus, claims 9 to 11 would lack inventive step in view of a combination of D1, D2 and D3, or further with D5 or D7.

## II-3. Claim 12

It is described in D5 that maximum anodization voltage of a sintered product of niobium powder is 200 V (page 1111, right column, Table I). This means that formation can be carried out at any voltage not higher than 200 V. Formation at a voltage of 30 to 50 volts would be a matter of routine design choice.

#### II-4. Claims 13 and 16-19

As explained in the above paragraph I-1, a niobium powder used for a capacitor anode having a BET specific surface area of at least  $0.5 \text{ m}^2/\text{g}$  is described in D1 (larger than about  $0.58 \text{ m}^2/\text{g}$ , presumably about  $1.5 \text{ m}^2/\text{g}$ ; Example 11, column 11, bottom two lines), D2 (larger than the range of about  $3.5 \text{ m}^2/\text{g}$  to about  $14.0 \text{ m}^2/\text{g}$ ; page 2, right lower column, lines 4-5 [Translation, page 4, lines 23-25]), and D3 ( $4.8 \times 10^4 \text{ m}^2/\text{kg}$  [=48  $\text{m}^2/\text{g}$ ]; page 469, right column, Table 7).

Claims 13 and 16-19 would lack inventive step in view of D1, D2, D3 and D5.

#### II-5. Claim 15

D6 discloses that a niobium powder used for the preparation of a capacitor anode is agglomerated (claim 2, col. 4, lines 61-61; and col. 2, lines 31-34).

Claim 15 would lack inventive step in view of a combination of D1, D2, D3, D5 and D6.

#### II-6. Claim 21

It is specifically disclosed in D1 to use a niobium powder having an average particle diameter of  $1.2 \text{ }\mu\text{m}$  (a specific surface area of at least about  $0.58 \text{ m}^2/\text{g}$  (presumably about  $1.5 \text{ m}^2/\text{g}$ ); see the above-paragraph I-1) and a bulk density of  $0.67 \text{ g/cm}^3$  (D1, column 11, line 67 to column 12, line 2) to provide an anode having a DC leakage of  $1.7 \text{ nA/CV}$  (see the above-paragraph I-1).

D3 discloses an ultrafine niobium power having a specific surface area of  $4.8 \times 10^4 \text{ m}^2/\text{kg}$  [=48  $\times \text{m}^2/\text{g}$ ], which has a bulk density of  $19 \text{ kg/m}^3$  [=0.019  $\text{g/cm}^3$ ] (D3, page 469, right column, Table 7).

Claim 21 would lack inventive step over a combination of D1, D2 and D3 with D5.

## II-7. Claims 22-24

D6 teaches that an anode of improved electrical capacitance and reduced D.C. leakage is prepared by the addition in columbium (i.e., niobium) powder of phosphorus-containing materials in amounts from about 5 to about 600 ppm based on elemental phosphorus (D6, Abstract; col. 1, lines 48-50; col. 2, lines 14-20).

Thus, claims 22 to 24 would lack inventive step over a combination of D1, D2, D3 and D5 with D6.

## II-8. Claims 25-28

The niobium powders specifically disclosed in Examples 1 and 2 of D2, which are mentioned above as having a specific surface area meeting the requirements of claims 1 and 2 in paragraph I-1, contains oxygen in amounts of 5.6% (=56,000 ppm) (Example 1 [Translation, page 5, line 28]), and 8% (=80,000 ppm) (Example 2 [Translation, page 6, line 9]). These oxygen contents in D2 meet "oxygen content of not less than 2,000 ppm" stipulated in claim 25.

D7 teaches the use of a niobium powder having an oxygen content of 0.5 to 1.4%, that is to say of 5,000 to 14,000 ppm as a starting material for making a capacitor anode (col. 1, lines 11-14, and col. 2, lines 32-35). These oxygen contents in D7 meet the oxygen contents of not less than 2,000 ppm, 2,000 to 20000 ppm, 2750 to 10000 ppm, and 4000 to 9000 ppm, stipulated in claims 25, 26, 27 and 28, respectively.

## III. Anticipation and Obviousness of Claims 29-30 directed to a capacitor

### III-1 Claims 29 and 30 lack novelty over D1

D1 discloses a process for preparing a niobium or tantalum powder, and teaches the use of the niobium or tantalum powder for an anode of electrolytic capacitor (col. 1, lines 10-20; Abstract).

As mentioned above in paragraph I-1, the capacitor anodes as claimed in claims 1 and 2 of Cabot EP 946,323 are clearly anticipated by the anode specifically disclosed in

Example 11 of D1 (columns 11-12). Therefore, the "capacitor" and "electrolytic capacitor" as claimed in claims 29 and 30, respectively, are also anticipated by D1.

III-2 Claims 29 and 30 lack inventive step over a combination of D1, D2, D3, D4 and D5.

The anodes as claimed in claims 1 to 7 are obvious from a combination of D1, D2, D3, D4 and D5 as mentioned above in paragraphs I-1 through I-4.

D1 teaches the use of niobium anode for an electrolytic capacitor (col. 1, lines 15-20; Abstract). D4 teaches the preparation of a capacitor with an anode made from a niobium powder (columns 14-16, Table 8-1, especially penultimate line in Table 8-1). D5 teaches application of niobium powder in the production of anodes for electrolytic capacitors (page 1111, left column, lines 2-4).

Therefore, claims 29 and 30 are also obvious from a combination of D1, D2, D3, D4 and D5.

IV. Anticipation and Obviousness of Claims 31-33 directed to use of a niobium powder for a capacitor anode

IV-1 Claims 31-33 lack novelty over D1

The same grounds as mentioned above in paragraph III-1 should apply.

IV-2 Claims 31-33 lack inventive step over a combination of D1, D2, D3, D4 and D5.

The same grounds as mentioned above in paragraph III-2 should apply.



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